# UNCLASSIFIED

AD 274 637

Reproduced by the

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.



# WATERTOWN ARSENAL LABORATORIES

APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION TECHNIQUE TO ANALYSIS OF IRON, TITANIUM, VANADIUM, AND ZIRCONIUM ALLOYS

TECHNICAL REPORT WAL TR 823.5/1

BY

FRED G. HOWELL

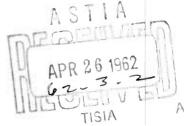
AND

WILLIAM K. MURRAY

DATE OF ISSUE - MARCH 1962

OMS CODE 5010.11.842
MATERIALS FOR ARMY WEAPONS AND COMBAT MOBILITY
D/A PROJECT 593-32-007

WATERTOWN ARSENAL WATERTOWN 72, MASS.



Spectrographic analysis - emission

Metals, spectrographic analysis
Solution techniques

APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION TECHNIQUE TO ANALYSIS OF IRON, TITANIUM, VANADIUM, AND ZIRCONIUM ALLOYS

Technical Report WAL TR 823.5/1

Ву

Fred G. Howell

and

William K. Murray

Date of Issue - March 1962

OMS Code 5010.11.842
Materials for Army Weapons and Combat Mobility
D/A Project 593-32-007

WATERTOWN ARSENAL WATERTOWN 72, MASS.

#### WATERTOWN ARSENAL LABORATORIES

#### TITLE

APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION TECHNIQUE TO ANALYSIS OF IRON, TITANIUM, VANADIUM, AND ZIRCONIUM ALLOYS

#### ABSTRACT

A spectrographic-solution technique has been applied to the analysis of certain iron, titanium, vanadium and zirconium alloys. The samples, after dissolution in an appropriate acid, are excited with a high-voltage spark using a commercial rotating-disk unit. Suitable line pairs are selected and calibration curves drawn using synthetic alloy solutions prepared from pure metals. The coefficient of variation for analysis of representative samples of each of the above alloy systems was determined.

FRED G. HOWELL Chemist (Anal)

William Y. / Murray

Supervisory Chemist (Anal)

APPROVED:

J. F. SULLIVAN

Director

atertown Arsenal Laboratories

#### CONTENTS

Pag	zе
ABSTRACT	
INTRODUCTION	3
EXPERIMENTAL	
Selection of Line Pairs	3
Preparation of Analytical Curves	4
GENERAL PROCEDURE	1
Apparatus	4
Reagents	5
Excitation rarameters	5
Electrode System	5
Exposure Procedure	5
Photographic Processing	6
RECOMMENDED PROCEDURES	
Determination of Manganese in Iron	6
Determination of Zirconium in Titanium	7
Determination of Titanium in Vanadium	8
	9
	1
	L2
	13
THEOLOGICAL OF THEOLOGICAL CONTRACTOR OF THE CONTRACTOR OF T	
CONCLUSIONS	14
TABLES	15
PEFFRENCES	18

#### INTRODUCTION

Many varied materials can be analyzed by preparing a solution of the sample and then analyzing the solution spectrographically. This technique is particularly effective when dealing with unusual metals or with a small lot of samples for which it is not practical to set up procedures which are unfamiliar to the "wet" chemist. This report describes six determinations which were performed by the spectrographic-solution technique. The approach to the development of the method is similar in each case. The samples were dissolved with appropriate acids, and synthetic standard solutions corresponding to the unknown samples exactly in composition and amount of acid present were prepared. These solutions were position and amount of acid present were prepared. These solutions were then excited spectrographically. The spectra were examined for suitable line pairs, modifications were made in the techniques, if required, to achieve the necessary accuracy, and, finally, calibration curves were prepared from the data.

#### EXPERIMENTAL

### A. Selection of Line Pairs

In selecting line pairs for spectrochemical procedures, a line pair is considered to be well matched if the excitation potentials are nearly equal for both the analytical line of the element being determined and the internal standard line of the base element. A well-matched pair is less affected by variations in excitation parameters.

Even after selection of possible line pairs on the basis of excitation potentials and other factors, it is still necessary to check to determine if the intensity ratios of the lines remain essentially constant under experimental conditions. In order to minimize the amount of data needed for selection of the best line pairs, some parameter which affects the intensity ratios can be deliberately varied beyond its normal experimental range. Frisque in a study of matrix effects varied the matrix and decided that the major cause of the changes in intensity ratios was due to temperature variations in the discharge.

Experimentally it is easier to vary the temperature of the discharge by varying the length of the analytical gap. This was done by Mahoney who found that the analytical curves underwent parallel horizontal shifts as the length of the spark gap (and temperature) varied if the lines were not well matched. Consequently, it is simple to employ the constancy in the intensity ratio of the line pairs as the discharge gap is varied as a measure for matching the lines.

For the alloy systems under study, it was necessary to select suitable line pairs experimentally, since none were available in the literature. Trial exposures of the various alloy systems were made to establish optimum exposure times for covering the concentration range of the minor

constituent. For the minor constituents, only the more sensitive arc or spark lines were visible and their excitation potentials were available in the literature. Among the matrix element lines, only the weaker ones had proper transmittances, within the desirable range of 20 to 60 percent, for use as internal standard lines. Excitation potentials were not available for most of these matrix lines.

To determine what line pairs would be well matched, exposures were made in duplicate, first with an analytical gap of 3 mm, then with a gap of 5 mm. The log intensity ratios were calculated for each tentative line pair. Those line pairs that showed the least change in ratio for the two gap widths were chosen for further study.

Standard solutions covering the desired range of concentration were sparked and those line pairs giving the best analytical curves were chosen to complete this investigation.

### B. Preparation of Analytical Curves

The transmittances of the selected alloy and internal standard line pairs from each set of standard solutions were converted to log intensity values by reference to the emulsion calibration curve. In Eq. (Ia = intensity of alloy line; Ib = intensity of internal standard line.)

Semi-logarithmic paper was used for preparing analytical curves by plotting the concentration of the alloying element on the log axis versus the ratio of log intensities (log  $\rm I_a/\rm I_b$ ) on the linear scale.

#### GENERAL PROCEDURE

#### A. Apparatus

The apparatus employed for this investigation is as follows:

Specorograp.	Baird Associates 3-meter concave grating instrument in Eagle mounting, with a reciprocal linear dispersion of 5.5 A
	per mm.

Excitation Source Jarrell-Ash Co. Custom Varisource, Model No. 4075.

Microphotometer Jarrell-Ash Co. Non-Recording Microphotometer eter and Comparator, Model No. 2100.

Rotating-Disk Unit Spex Industries, Inc. Speed of rotation is 10 rpm.

Plate Processor

Jarrell-Ash Co. Photoprocessor,

Model No. 3410.

Spectrographic Plates

Eastman Kodak Spectrum Analysis Plates No. 1, 4 inches by 10 inches.

Teflon Cups

Machined from Teflon disks l inch in diameter and 3/8 inch thick.

#### B. Reagents

Standard solutions were prepared as described under the various determinations performed.

Metals of the highest purity obtainable should be used in making up standard solutions. If the best grade of metal available is contaminated with the element being determined, the impurity should be determined chemically or by the method of Ahrens.4

## C. Excitation Parameters

The following settings on the Varisource were used for exciting the samples:

### D. Electrode System

A high-purity graphite disk 1/2 inch in diameter and 1/8 inch thick rotates in a vertical plane perpendicular to the optical axis. The disk rotates at 10 rpm with its lower edge in contact with the solution contained in a Teflon cup. The upper or counter electrode is a graphite rod 1/4 inch in diameter and 2 inches long, pointed to a cone of 120 degrees included angle and spaced 4.0 mm above the upper edge of the disk.

## E. Exposure Procedure

The following steps were involved in the exposure procedure:

- 1. Make duplicate exposures of both standard and unknown samples.
- 2. Fill the Teflon cup with the solution to be analyzed, using a plastic dropping pipet for solutions containing hydrofluoric acid.

- 3. Place the cup on the platform of the rotating-disk assembly and adjust the disk so that it rotates freely partially immersed in the solution without touching the cup.
- 4. Center the counter electrode directly above the rotating disk and adjust the gap to 4.0 mm.
- 5. Make the exposures using the exposure conditions listed under each determination.

#### F. Photographic Processing

The photographic processing included the following steps:

- 1. Process the Eastman S. A. No. 1 plates at a temperature of 70 F.
- 2. Develop in Kodak D-19 developer for 4-1/2 minutes, then place in an acetic acid (5%) short-stop bath for 20 seconds.
- 3. Fix the plates for 5 minutes in Kodak Rapid Fixer and wash for 5 minutes in running water.
  - 4. Rinse with distilled water and dry with a warm air blower.

#### G. Photometry

Measure the percent transmittance of the analytical line pairs on the developed plates with the microphotometer using a slit 5 microns wide and 1.2 mm long.

#### RECOMMENDED PROCEDURES

### Determination of Manganese in Iron

This method is recommended for the analysis of manganese in iron in the range from 0.001 to 0.02 percent.

### A. Preparation of Standard Solutions

1. Iron Stock Solution (50 mg of Fe per ml)

Dissolve 10 grams of iron, which is spectroscopically free from manganese, in 150 ml of HCl (1:1). Oxidize with a minimum of HNO<sub>3</sub>, cool, transfer to a 200-ml volumetric flask, and dilute to volume with HCl (1:1).

2. Manganese Stock Solution (0.10 mg of Mn per ml)

Dissolve 10.0 mg of pure manganese metal in HCl (1:1). Transfer to a 100-ml volumetric flask and dilute to volume with HCl (1:1).

3. Manganese Stock Solution (0.01 mg of Mn per ml)

Transfer 10.0 ml of the manganese stock solution (0.10 mg of Mn per ml) to a 100-ml volumetric flask and dilute to volume with HCl (1:1).

## 4. Standard Working Solutions of Manganese in Iron

Transfer 20-ml aliquots of the iron stock solution (50 mg of Fe per ml) to each of six 50-ml Erlenmeyer flasks numbered from 1 to 6.

To flasks 1, 2, and 3 add 1.0, 2.0, and 5.0 ml, respectively, of the manganese stock solution (0.01 mg of Mn per ml). To flasks 4 and 5 add 1.0 and 2.0 ml, respectively, of the manganese stock solution (0.10 mg of Mn per ml).

Add HCl (1:1) to each of the six flasks so that each solution will have a volume of 25 ml.

The standard working solutions now represent iron solutions containing 0.000, 0.001, 0.002, 0.005, 0.010, and 0.020 percent manganese.

#### B. Preparation of Samples

Transfer 1-gram samples of iron alloy to 50-ml Erlenmeyer flasks and add 20 ml of HCl (1:1). Heat gently until dissolved. Oxidize by the dropwise addition of  $HNO_3$ . Cool, dilute to 25  $\pm$  1 ml with HCl (1:1).

#### C. Exposure Conditions

The following represent the exposure conditions:

	-104 2704	and and an
Spectral region, angstroms	2405-3105,	2nd order
Slit width, microns	25	
Plate line-mask width, mm	2	
Spark preburn period, sec	15	
Spark exposure period, sec	40	
Manganese line, angstroms	2576.10	
Iron line, angstroms	2565.07*	

#### D. Analytical Curves

Prepare as described under EXPERIMENTAL, Section B.

## Determination of Zirconium in Titanium

This method is recommended for the analysis of zirconium in titanium and titanium alloys at the 2 to 8 percent level.

## A. Preparation of Standard Solutions

1. Accurately weigh 20, 40, 60, and 80 milligrams of pure zirconium metal and transfer each to a 100-ml plastic dropping bottle. Add to each dropping bottle accurately weighed portions of pure titanium metal so that the total weight of the zirconium and titanium in each bottle is one

\* This line is not listed in the M.I.T. Wavelength Tables<sup>5</sup>

- 2. Add 10 ml of water to each of the four bottles and then 10 ml of HF slowly. Add 10 ml of HCl and digest in a hot water bath until the samples are completely dissolved. Oxidize the solutions with 1 ml of HNO3, cool, and dilute to 50 ml with water. Place cover containing dropping pipet on each bottle.
- 3. Correct the standard solutions for any zirconium present in the titanium base metal (see GENERAL PROCEDURE, Section B). The standard solutions will now represent 2, 4, 6, and 8 percent zirconium plus any zirconium present in the base metal.

### B. Preparation of Samples

Transfer 1-gram samples of titanium alloy to 100-ml plastic dropping bottles. Dissolve the samples as described under Preparation of Standard Solutions of Zirconium in Titanium, Paragraph 2.

### C. Exposure Conditions

re condite some	laco lat order
Spectral region, angstroms	2750-4100, 1st order
Slit width, microns	25
Plate line-mask width, mm	2
Spark preburn period, sec	15
Spark exposure period, sec	30
Zirconium lines, angstroms	3095.07
Titanium line, angstroms	3096.42

### D. Analytical Curves

Prepare as described under EXPERIMENTAL, Section B.

## Determination of Titanium in Vanadium

This method is recommended for the analysis of titanium in vanadium at the 0.02 to 0.5 percent level.

## A. Preparation of Standard Solutions

1. Titanium Stock Solution (0.50 mg of Ti per ml of HCl (1:1)).

Transfer 100.0 mg of pure titanium metal to a 200-ml volumetric flask.

Add 100 ml of HCl (1:1), place the flask in a beaker of boiling water, and heat until the titanium is completely dissolved.

Remove the flask, cool, and dilute to volume with HCl (1:1).

2. Standard Working Solutions of Titanium in Vanadium

Transfer six 2-gram samples of pure vanadium to six 100-ml plastic dropping bottles.

Add 10 ml of HF to each bottle, and then add 2 ml of HNO3 dropwise. Keep the bottles immersed in cold water to moderate the reaction, and let stand until the vanadium is dissolved.

To five of the bottles add 0.4, 1.0, 2.0, 4.0, and 10.0 ml of the titanium stock solution (0.50 mg of Ti per ml of HCl,(1:1)).

Add HCl (1:1) to each of the six bottles to bring the total amount of HCl (including the HCl that was added with the titanium stock solution) to 40 ml. The total volume will be approximately 50 ml.

Correct the standard working solutions for any titanium in the vanadium base metal. The standard solutions will now represent 0.02, 0.05, 0.10, 0.20, and 0.50 percent titanium plus any titanium present in the base metal.

## B. Preparation of Samples

Transfer 2-gram samples of vanadium alloy to 100-ml plastic dropping bottles.

Add to each bottle 10 ml of HF and then 2 ml of HNO3 dropwise, controlling the speed of the reaction by immersing the bottles in a cold water bath, and let stand until the samples are dissolved.

Add 40 ml of HCl (1:1) to each. The total volume will be approximately 50 ml.

## C. Exposure Conditions

re Conditions	2750-4100, 1st order	
Spectral region, angstroms		
Slit width, microns	25	
Plate line-mask width, mm	2	
Spark preburn period, sec	15	
Spark exposure period, sec	15	
	3349.04	
Titanium line, angstroms	3376.06	
Vanadium line, angstroms		

## D. Analytical Curves

Prepare as described under EXPERIMENTAL, Section B.

# Determination of Cobalt in Zirconium

This method is recommended for the analysis of cobalt in zirconium and zirconium alloys at the 0.01 to 0.50 percent level.

### A. Preparation of Standard Solutions

### 1. Cobalt Stock Solution (1 mg of Co per ml)

High-purity cobalt comes in small chunks very difficult to break up. A small weighed chunk of cobalt is dissolved in HCl(1:1) and transferred to a volumetric flask of suitable size and made up to volume with HCl(1:1). A volume containing 100 mg of Co is measured by means of a buret or pipet into a 100-ml volumetric flask and made up to volume with HCl(1:1).

## 2. Standard Working Solutions of Cobalt in Zirconium

Accurately weigh seven 2-gram samples of pure zirconium metal and transfer each to a 100-ml plastic dropping bottle.

Add 10 ml of water to each and dissolve the zirconium by the slow addition of 5 ml of HF. When dissolution is complete, dilute to 40 ml with water. Add to six of the bottles 0.2, 1.0, 2.0, 4.0, 7.0, and 10.0-ml aliquots of a standard cobalt solution (1 mg of Co per ml). Add HCl (1:1) to each of the seven bottles to bring the final volume to 50 ml.

Correct the standard solutions for any cobalt in the zirconium base metal. The standard solutions now represent 0.01, 0.05, 0.1, 0.2, 0.35, and 0.50 percent cobalt plus any cobalt present in the base metal.

### B. Preparation of Samples

Transfer 2-gram samples of zirconium alloy to 100-ml plastic dropping bottles. Dissolve in HF as described under Standard Working Solutions of Cobalt in Zirconium. Add 10 ml of HCl (1:1) to each bottle and dilute to 50 ml with water.

#### C. Exposure Conditions

3410	
Spectral region, angstroms	2750-4100, 1st order
Slit width, microns	25
Plate line-mask width, mm	2
Spark preburn period, sec	15
Spark exposure period, sec Cobalt less than 0.05% Cobalt greater than 0.05%	45 35
Cobalt line, angstroms	3453.51
Zirconium line, angstróms	3370.59

#### D. Analytical Curves

Prepare curves as described under EXPERIMENTAL, Section B.

### Determination of Iron in Zirconium

This method is recommended for zirconium and zirconium alloys containing 0.05 to 0.25 percent iron.

## A. Preparation of Standard Solutions

## 1. Iron Stock Solution (0.5 mg of Fe per ml)

Pipet 1 ml of iron stock solution (50 mg of Fe per ml) (as described in Section A l for the determination of manganese in iron) into a 100-ml volumetric flask and dilute to volume with HCl (1:1).

## 2. Standard Working Solutions of Iron in Zirconium

Accurately weigh five 2-gram samples of pure zirconium metal and transfer each to a 100-ml plastic dropping bottle.

Add 10 ml of water to each bottle and dissolve the zirconium by the slow addition of 5 ml of HF to each. When dissolution is complete, dilute to 40 ml with water. To four of the bottles add 2.0, 4.0, 6.0, and 10.0-ml aliquots of a standard iron solution (0.5 mg of Fe per ml). Add HCl (1:1) to each of the five bottles to bring the final volume to 50 ml.

Correct the standard solutions for any iron in the zirconium base metal. The standard solutions now represent 0.05, 0.10, 0.15, and 0.25 percent iron plus any iron present in the base metal.

### B. Preparation of Samples

Transfer 2-gram samples of zirconium alloy to 100-ml plastic dropping bottles. Dissolve in HF as described under Standard Working Solutions of Iron in Zirconium. Add 10 ml of HCl (1:1) to each and dilute to 50 ml with water.

### C. Exposure Conditions

	2405-3105,	and order
Spectral region, angstroms	2405-3105,	Zild Oldel
Slit width, microns	25	
Plate line-mask width, mm	2	
Spark preburn period, sec	15	
Spark exposure period, sec	20	
-	2973.17	
Iron line, angstroms	2973.69*	
Zirconium line, angstroms	2913.07	

<sup>\*</sup> Not listed in the M.I.T. Wavelength Tables. Listed in the Oak Ridge Table.6

#### D. Analytical Curves

Prepare curves as described under EXPERIMENTAL, Section B.

### Determination of Vanadium in Zirconium

This method is recommended for the analysis of vanadium in zirconium and zirconium alloys at the 0.05 to 0.35 percent level.

### A. Preparation of Standard Solutions

## 1. Vanadium Stock Solution (1 mg of V per ml)

Weigh 100 mg of high-purity vanadium metal into a 100-ml beaker, add 5 ml of HNO<sub>3</sub> to dissolve and heat gently to complete dissolution. Add about 50 ml HCl (1:1) and transfer to a 100-ml volumetric flask. Dilute to volume with HCl (1:1).

### 2. Standard Working Solutions of Vanadium in Zirconium

Accurately weigh six 2-gram samples of pure zirconium metal and transfer each to a 100-ml plastic dropping bottle.

Add 10 ml of water to each bottle and dissolve the zirconium by the slow addition of 5 ml of HF. When dissolution is complete, dilute to 40 ml with water. To five of the bottles add 1.0, 2.0, 3.0, 5.0, and 7.0-ml aliquots of a standard vanadium solution (1 mg of V per ml). Add HCl (1:1) to each of the six bottles to bring the final volume to 50 ml.

Correct the standard solution for any vanadium in the zirconium base metal. The standard solutions now represent 0.05, 0.10, 0.15, 0.25, and 0.35 percent vanadium plus any vanadium present in the base metal.

#### B. Preparation of Samples

Transfer 2-gram samples of zirconium alloy to 100-ml plastic dropping bottles. Dissolve in HF as described under Standard Working Solutions of Vanadium in Zirconium. Add 10 ml of HCl (1:1) to each and dilute to 50 ml with water.

#### C. Exposure Conditions

are comme	
Spectral region, angstroms	2750-4100, 1st order
Slit width, microns	25
Plate line-mask width, mm	2
Spark preburn period, sec	15
Spark exposure period, sec	30
Vanadium line, angstroms	3118.38
Zirconium line, angstroms	3115.72

#### D. Analytical Curves

Prepare curves as described under EXPERIMENTAL, Section B.

#### PRECISION OF RESULTS

The precision of the foregoing determinations was checked by running representative samples of each alloy system ten times on one spectrographic plate.

One sample solution of each alloy was prepared as described under each alloy. Five portions of each solution were then taken for analysis. This procedure eliminated the possibility of error due to segregation in the alloys. Two exposures were made with each portion of the sample solution, changing the electrodes between each exposure. This was in accord with the usual analytical technique employed.

The standard deviation  $(\sigma)$  was determined using the formula:

$$\sigma = \sqrt{\frac{\sum (X_1 - \overline{X})^2}{n - 1}}$$

where  $X_1$  = percent of the element determined from each exposure

 $\overline{\chi}$  = average of ten percentages determined

n = number of exposures

The coefficient of variation (v) is calculated from the formula:

$$v = \frac{\sigma}{\overline{X}} \times 100$$

Tables I through VI show the actual percentages obtained for each run of the samples. The coefficient of variation ranges from 0.57 percent for iron in zirconium to 6.57 percent for titanium in vanadium. The 0.57 value is probably lower than could be obtained consistently with this procedure, and likewise the 6.57 percent value should be capable of being lowered with more experience or slight changes in technique.

The coefficient of variation does not necessarily measure the accuracy of a determination. In the spectrographic analysis of solids, variations in the matrix composition or condition can cause the accuracy to be much less than the precision as measured by the coefficient of variation. It was not possible in this work to measure the accuracy directly since no samples of accurately known analysis were available. However, the advantage of solution techniques is that all variation due to matrix composition

and past history can be eliminated if the synthetic reference solutions are prepared to correspond exactly to the sample solutions. In the case of the binary alloys analyzed in this report the preparation of synthetic standards corresponding exactly to the samples was possible. The largest source of error was in the analysis of the "pure" elements used to prepare the synthetic standards. If the analysis of these elements was exact, the accuracy of the determinations should be equal to the precision which was found.

#### CONCLUSIONS

Spectrographic-solution analytical techniques can be successfully applied to the determination of many metallic elements in various base metals. When this method is applicable, reasonable accuracy can be obtained in the analysis of unusual alloys with a minimum of time and difficulty.

TABLE I
REPEATABILITY OF MANGANESE DETERMINATION IN IRON

Exposure No.	Manganese, $%$	Difference $(X_1 - \overline{X})$
1	0.0156	00038
2	0.0160	+.00002
3	0.0163	+.00032
4	0.0158	00018
5	r.0163	+.00032
6	0.0156	00038
7	0.0160	+.00002
8	0.0158	00018
9	0.0161	+.00012
10	0.0163	+.00032

Average  $(\overline{X}) = 0.01598$ 

Standard deviation = 0.00027

Coefficient of variation = 1.72%

NOTE: Sample was NBS Ingot Iron Standard 55c, certified as containing 0.016% Mn

TABLE II

REPEATABILITY OF ZIRCONIUM DETERMINATION IN TITANIUM

Exposure	Zirconium,% (X <sub>1</sub> )	Difference $(X_1 - \overline{X})$
1	4.83	131
2	5.13	+.169
3	5.02	+.059
4	5.04	+.079
5	5.00	+.039
6	5.00	+.039
7	4.87	091
8	5.00	+.039
9	4.85	111
10	4.87	091

Average  $(\overline{X}) = 4.961$ 

Standard deviation = 0.0994

Coefficient of variation = 2.00%

NOTE: Sample was MR 336, 5% Zr in Ti, nominal analysis

TABLE III REPEATABILITY OF TITANIUM DETERMINATION IN VANADIUM

Exposure	Titanium, $\chi$	Difference $(X_1 - \overline{X})$
1	0.321	+.0257
2	0.280	0153
3	0.320	+.0247
4	0.302	+.0077
5	0.299	+.0047
6	0.307	+.0117
7	0.304	+.0087
8	0.264	0313
9	0.280	0153
10	0.276	0193
10	•	

Average  $(\overline{X}) = 0.2953$ 

Standard deviation = 0.0194

Coefficient of variation = 6.57%

NOTE: Sample was MR 347, 0.3% Ti in V, nominal analysis

TABLE IV REPEATABILITY OF COBALT DETERMINATION IN ZIRCONIUM

Exposure	Cobalt,% (X <sub>1</sub> )	Difference $(X_1 - \overline{X})$
1	0.0495	00106
2	0.0520	+.00144
3	0.0482	00236
4	0.0497	00086
5	0.0512	+.00064
6	0.0533	+.00274
7	0.0502	00036
8	0.0502	00036
9	0.0500	00056
10	0.0513	+.00074
TO		

Average  $(\overline{X}) = 0.0506$ 

Standard deviation = 0.00144

Coefficient of variation = 2.84%

NOTE: Sample was MR 672, 0.05% Co in Zr, nominal analysis

TABLE V REPEATABILITY OF IRON DETERMINATION IN ZIRCONIUM

Exposure	Iron,% (X <sub>1</sub> )	$\begin{array}{c} \text{Difference} \\ (X_1 - \overline{X}) \end{array}$
1	0.150	+.0005
2	0.149	0005
3	0.149	0005
4	0.149	0005
5	0.149	0005
6	0.150	+.0005
7	0.150	+.0005
8	0.151	+.0015
9	0.148	0015
10	0.150	+.0005

Average  $(\overline{X}) = 0.1495$ Standard deviation = 0.00085

Coefficient of variation = 0.57%

NOTE: Sample was MR 670, 0.15% Fe in Zr, nominal analysis TABLE VI

REPEATABILITY OF VANADIUM DETERMINATION IN ZIRCONIUM

Exposure No.	Vanadium, $\%$	Difference $(X_1 - \overline{X})$
1	0.122	+.0089
2	0.110	0031
3	0.117	+.0039
7	0.112	0011
5	0.117	+.0039
6	0.102	0111
7	0.115	+.0019
8	0.112	0011
9	0.112	0011
10	0.112	0011
<del>-</del> -		

Average  $(\overline{X}) = 0.1131$ Standard deviation = 0.00528

Coefficient of variation = 4.67%

NOTE: Sample was MR 664, 0.1% V in Zr, nominal analysis

#### REFERENCES

- 1. FRISQUE, A. J., Causes and Control of Matrix Effects in Spectrographic Discharges, Analytical Chemistry, v. 32, 1960, p. 1484.
- 2. MAHONEY, BERNARD L., JR., The Effects of Parameter Variations on the Spectrochemical Analysis of Low-Alloy Steels, Watertown Arsenal Laboratories Technical, Note WAL TN 823/1, May 1961.
- 3. AMERICAN SOCIETY FOR TESTING MATERIALS, Methods for Emission Spectrochemical Analysis, Philadelphia, 1960.
- 4. AHRENS, L. H., and TAYLOR, S. R., Spectrochemical Analysis, 2nd Edition, Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, ch. 11-4, 1961, p. 154.
- 5. HARRISON, G. R., Massachusetts Institute of Technology Wavelength Tables, John Wiley and Sons, Inc., New York, 1939.
- 6. NORRIS, JOHN A., Wavelength Table of Rare-Earth Elements and Associated Elements Including Zirconium, Thorium, Hafnium, Rhenium, and Tellurium, Oak Ridge National Laboratory Report ORNL-2774, February 1960.

#### WATERTOWN ARSENAL WATERTOWN 72, MASSACHUSETTS

#### TECHNICAL REPORT DISTRIBUTION

Title: Applications of a Spectrographic-

Report No.: WAL TR 823.5/1 Solution Technique to Analysis of March 1962 Iron, Titanium, Vanadium and Zirconium Alloys Distribution List approved by Ordnance Materials Research Office, 30 October 1961. No. of TO Copies Director of Defense Research and Engineering, Room 3D-1067, The Pentagon, Washington 25, D. C. ATTN: Mr. J. C. Barrett 1 Advanced Research Project Agency, The Pentagon, Washington 25, D.C. ATTN: Dr. G. Mook 1 Defense Metals Information Center, Battelle Memorial Institute, 1 Columbus, Ohio Solid Propellant Information Agency, The Johns Hopkins University, Silver Spring, Maryland ATTN: Applied Physics Laboratory 3 Commander, Armed Services Technical Information Agency, Arlington Hall Station, Arlington 12, Virginia ATTN: TIPDR 10 Commander, Army Research Office, Arlington Hall Station, 1 Arlington 12, Virginia

Chief of Ordnance, Department of the Army, Washington 25, D. C.

ATTN: ORDTB - Research and Development Division 1

Commanding General, Aberdeen Proving Ground, Maryland ATTN: C&CL, Dr. C. Pickett 1

Commanding General, Ordnance Tank-Automotive Command, Detroit 9, Michigan

ATTN: ORDMC-IF-2, Mr. S. Sobak 1

Commanding General, Ordnance Weapons Command, Rock Island, Illinois ATTN: ORDOW-IA, Mr. B. Gerke 1

Commanding General, U. S. Army Ballistic Missile Agency, Redstone Arsenal, Alabama

ATTN: Dr. G. H. Reisig 1

ORDAB-RPEM, Mr. P. B. Wallace 1

Documentation and Technical Information Branch 2

ORDAB-IEE

No. of TO Copies Commanding General, U. S. Army Ordnance Missile Command, Redstone Arsenal, Alabama ATTN: ORDMX-RME-AE, Lt. E. J. Wilson 1 Commanding General, U. S. Army Rocket and Guided Missile Agency, Redstone Arsenal, Alabama ATTN: ORDXR-RGS, Mr. Robert Fink 1 ORDXR-IQI, Mr. W. H. Thomas 1 Commanding Officer, Frankford Arsenal, Philadelphia 37, Pennsylvania ATTN: ORDBA-1330, Dr. H. Gisser 1 ORDBA-1320, Mr. H. Markus 1 Commanding Officer, Ordnance Materials Research Office, Watertown Arsenal, Watertown 72, Massachusetts ATTN: RPD 1 Commanding Officer, Picatinny Arsenal, Dover, New Jersey ATTN: Mr. J. J. Scavuzzo, Plastics and Packaging Laboratory 3 ORDBB-DE3, Mr. D. Stein 1 Commanding Officer, PLASTEC, Picatinny Arsenal, Dover, New Jersey 1 Commanding Officer, Rock Island Arsenal, Rock Island, Illinois ATTN: Materials Section, Laboratory 1 Commanding Officer, Springfield Armory, Springfield 1, Massachusetts ATTN: Mr. R. Korytoski, Research Materials Laboratory 1 Commanding Officer, Watervliet Arsenal, Watervliet, New York ATTN: ORDBF-RR, Mr. F. Dashnaw 1 Headquarters, U. S. Army Signal R&D Laboratory, Fort Monmouth, N.J. ATTN: SIGRA/SL-XE, Mr. H. H. Kedesky 1 Chief of Research and Development, U. S. Army Research and Development Liaison Group, APO 757, New York, N. Y. ATTN: Dr. B. Stein 1 Chief, Bureau of Naval Weapons, Department of the Navy, Room 2225, Munitions Building, Washington 25, D. C. ATTN: RMMP 1 Office of Naval Research, Department of the Navy, Washington 25, D.C. ATTN: Code 423 1 Special Projects Office, Department of the Navy, Washington 25, D. C. ATTN: SP 271 1 Commander, U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland ATTN: Code WM 1

No. of TO Copies Commander, U. S. Naval Ordnance Test Station, China Lake, California ATTN: Technical Library Branch Commander, U. S. Naval Research Laboratory, Anacostia Station, Washington 25, D. C. ATIN: Mr. J. E. Srawley 1 U. S. Air Force Directorate of Research and Development, Room ND-313, The Pentagon, Washington 25, D. C. ATTN: Lt. Col. J. B. Shipp, Jr. 1 Wright Air Development Division, Wright Patterson Air Force Base, Ohio ATTN: ASRCEE-1, H. Zoeller 2 ARDC Flight Test Center, Edwards Air Force Base, California ATTN: FIRSC, Solid Systems Division 5 AMC Aeronautical Systems Center, Wright Patterson Air Force Base, Ohio ATTN: LMBMO, Manufacturing and Materials Technology Division 2 Headquarters, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio ATTN: ASRCEM-1, Mr. Klinger 2 National Aeronautics and Space Administration, Washington, D. C. ATTN: Mr. R. V. Rhode 1 Mr. G. C. Deutsch 1 Mr. B. G. Achhammer 1 Dr. W. Lucas, George C. Marshall Space Flight Center, Huntsville, Alabama ATTN: M-S&M-M 1 Mr. William A. Wilson, George C. Marshall Space Flight Center, Huntsville, Alabama ATTN: M-F&AE-M 1 Dr. L. Jaffe, Jet Propulsion Laboratory, California Institute of 1 Technology, 4800 Oak Grove Drive, Pasadena, California Aerojet-General Corporation, Post Office Box 1168, Sacramento, California ATTN: Librarian 1 Aerojet-General Corporation, Post Office Box 296, Azusa, California ATTN: Librarian 1 Mr. C. A. Fournier 1

)

No. of Copies Allison Division, General Motors Corporation, Indianapolis 6, Indiana ATTN: Mr. D. K. Hanink 1 ARDE-Portland, Inc., 100 Century Road, Paramus, New Jersey ATTN: Mr. R. Alper 1 Atlantic Research Corporation, Shirley Highway and Edsall Road, Alexandria, Virginia ATTN: Mr. E. A. Olcott 1 Curtiss-Wright Corporation, Wright Aeronautical Division, Wood-Ridge, New Jersey ATTN: Mr. R. S. Shuris 1 Mr. A. M. Kettle, Technical Library 1 Hercules Powder Company, Allegheny Ballistics Laboratory, Post Office Box 210, Cumberland, Maryland ATTN: Dr. R. Steinberger 1 Hughes Aircraft Company, Culver City, California ATTN: Librarian 1 Tapco Group, 23555 Euclid Avenue, Cleveland 17, Ohio ATTN: Mr. W. J. Piper 1 Commanding Officer, Watertown Arsenal, Watertown 72, Massachusetts

ATTN: ORDBE-LXM, Technical Information Section

84 -- TOTAL COPIES DISTRIBUTED

Authors

5

2

UNCLASSIFIED	Watertown 72, MassSOLUTION TECHNIQUE ANABULM, AND ZIRONIUM analysis ism E. Hurray	el	has been applied 3. Solution techniques	with a high-voltage I. Howell, sign unit. Suitable Pred G.	thos curves dispared in Murray, pared from pure William K.	be above alloy III. OMS Code 5010.11.842	14.	ONCLASSIFIED	DIUTION TECHNIQUE 1. Spectrographic analysis — MD ZIROONIUM emission — K. Mutray Indiana — Massion — Massi	962, 18 pp tables, 2. Metals, 593-32-007, analysis	tanium, vanadium techniques atter dissolution	dwith a high-voltage I. Howell, disk usit. Suitable Pred G.	epared from pure II. Murray, on for analysis of William K.	the above alloy III. OHS Code 5010.11.842	IV. D/A Proj. 593-32-007	TATIONS
OTS Price \$0.50 Accession No.	AD Valentown Arsenal Laboratories, Watertown 72, Mass. APPLICATIONS OF A SPECTHOGRAPHIC-SOLUTION TECHNIQUE TO MALISIS OF IROW, TITANIUM, WANABIUM, AND ZIRONIUM, TOWARD AND MARKED AND ALLESS OF MARKET AND MARKET AND ALLESS OF THE ARCHITICAL TOWARD AND AND ALLESS OF THE ARCHITICAL TOWARD AND AND AND AND AND AND AND AND AND AN	ALLOUS FIELD ST. MAIL TR 823.5/1, Mar 1962, 18 pp - tables, QMS Code 5010.11.842 - D/A Project 593-32-007, Unclassified Report	A spectrographic-solution technique has been applied to the analysis of certain iron, titanium, wanadium	and airconium alloys. The samples, after dissolution in an appropriate acid, are excited with a bigh-voltage spark using a commercial rotating-disk unit. Suitable	line pairs are selected and calibration curves drome pare using synthetic alloy solutions prepared from pare	metals, the continues of each of the above alloy respect thive samples of each of the above alloy correspond and determined.	NO DISTRIBUTION LIMITATIONS	OTS Price \$0.50 Accession No.	Watertown Arsenal Laboratories, Watertown 72, Mass. Watertown Arsenal Laboratories Solution TECHNIGUE APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION TECHNIGUE TO ANALYSIS OF IRON, ITTANIUM, WARABULIM, REPORTED TO ANALYSIS OF IRON, ITTANIUM, WARABULIM, REPORTED TO ANALYSIS OF IRON, ITTANIUM, WARABULIM,	ALIOTS - Fred U. ROWELL AND MARCH 1962, 18 pp - tables, Report No. WAL TR 823.5/1, March 1962, 18 pp - tables, OMS Code 5010.11.842 - D/A Project 593-32-007,	Unclassified Keport A spectrographic-solution technique has been applied A spectrographic-solution technique has been applied to the analysis of certain iron, titanium, vanadium to the analysis of certain promises after	and incombum alloys, no seasons, and appropriate add are excited with a high-voltage snark using a commercial rotating-disk unit. Spitable	line pairs are selected and calibration curves treated town but using synthetic alloy solutions prepared from pure using synthetic alloy solutions prepared from pure	metals, the coernities of each of the above alloy representative samples of each of the above alloy systems was determined.		NO DISTRIBUTION LIMITATIONS
	UNCLASSIFIED  1. Specificgraphic	2 Metals,	analysis 3. Solution	I. Howell,	Fred G.	William K.			UNCLASSIFIED I. Spectrographic analysis	2. Metals,	analysis 3. Solution techniques	I. Bowell,		-	IV. D/A Proj.	040-05-040
Ore: Deice \$0.50	Accession No.  ACCESSION NO.  AMERICAN ALSENAL LABORATORIES, WATERTOWN 72, MASS. APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION TECHNIQUE TO APPLICATIONS OF A SPECTROGRAPHIC-SOLUTION AND ATRODUCE	ANALYSIS OF IRON, 111ANJUN, MARKELLOTS, Fred G. Rowell and William E. Murray Report No. Wal TR 823. A.J. Mar 1962, 18 pp - tables, Report No. Wal Tr. 949 - D/A Project 593-32-007.	OMS Code belo. 11.01. Unclassified Report A spectrographic-solution technique has been applied A spectrographic-solution technique has been applied	to the analysis of certain iron, after dissolution and zirconium alloys. The samples, after dissolution in an appropriate acid, are excited with a high-voltage in an appropriate acid, are interested unit. Suitable	spark using a commercial total the spark using a convex drawn line pairs are selected and calibration corves drawn line pairs are selected to solutions prepared from pure	ysis or loy		NO 1121111111111111111111111111111111111	AD Accession No.  AD Accession No.  AD Accession No.  Approximation 12, Mass.  Applications of A SPECTROGRAPHIC-SQLUTION TECHNIQUE TO APPLICATIONS OF A SPECTROGRAPHIC-SQLUTION TECHNIQUE TO A SPECTROGRAPHIC-SQLUTION TECHNIQUE TO A SPECTROGRAPHIC-SQLUTION TO A SPECTROGRAPHIC-SQLUTION TO A SPECTROGRAPHIC TO	ANALYSIS OF IRON, TITANIUM, NAMADIUM, AND ELECTRON ALLOTS - Fred G. Howell and William K. Murray Renort No. Wal TR 823.5/1, March 1962, 8, pp - tables,	OMS Code 5010.11.842 - D/A Project 350-32-00; Unclassified Report A spectrographic-solution technique has been applied	to the analysis of certain from titleatum, and an alloys alloy and zirconium alloys. The samples, after dissolution and zirconium alloys alloyed with a high-voltage	in an appropriate commercial rotating-disk unit. Suitable spark using a commercial rotating-disk unit. Suitable in pairs are selected and calibration curves drawn line pairs are selected and calibration curves drawn pure	using synthetic alloy solutions prepared in metalls. The coefficient of variation for abalishs of renessentative samples of each of the above alloy	systems was determined.	

AD  ACCESSION NO.  ACCESSION NO.  ACCESSION NO.  AND TRANS.  MATERIA OF A SPECINGENFHIC-SOLUTION TECHNICUS TO ANALYSIS OF 180N, TITANINH, VANABUUM, AND ZIRONIUH TO ANALYSIS OF 180N, TITANINH, VANABUUM, AND ZIRONIUH ALLOYS - Fred G. Howell and William E. Murray ALLOYS - Fred G. Howell and William E. Murray Report No. WAI TR 823.5/1, Mar 1962, 18 pp tables, ONS Code 5010, 11842 - D/A Project 593-32-007, Unclassified Report Out to analysis of certain iron, titasium, ranadium to the analysis of certain iron, titasium, ranadium and zironnium alloys. The samples, atter dissolution and performant acid, are excited with a high-orling in an appropriate acid, are excited with a high-orling in an appropriate acid, are excited with a high-orling in an appropriate acid, are excited with a high-orling in an appropriate acid, are acid, are analysis of representative samples, of cach of the above alloy representative samples of each of the above alloy representative samples of each of the above alloy ACCESSION NO DISTRIBUTION LIMITATIONS  NO DISTRIBUTION LIMITATION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION TECHNIQUE ACCESSION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION OF THE MATERIA CONTROLUCION OF A SPECTEGRAPHIC-SOLUTION OF THE MATERIA C	UNCLASSIFIED AD AD ACCESSION NO.  1. Spectrographic ADDITIONS OF A SPECIFOGRAPHIC. SOLUTION TECHNIC ADDITION TO ANINSTS OF 180N, 171ANIUM, VANABULM, AND ZERO anialism anialis	UNCLASSIFIED		•	es, 2 Metals, spectrographic	8	- e		111.	IV. D/A Proj. 693-32-007	UNCLASSIFIED	Mass.  1. Spectrographic analysis - emission	tables, 2 Metals, spectrographic analysis	-	roltage I. Howell, Fred G.	Ħ	Ħ	1V. D/A Proj. 693-32-007	
	Z Massadur zn zson	5 Price 50.50	AD Vatertows Arsenal Laboratories, Watertows 72, Mass.	APPLICATIONS OF A SPECTROGRAPHIC SOCIETY OF A NAISTS OF INDO. TITANIUM, VANABUUM, INDICATION TO ANAISTS OF HOWELL AND WILLIAM K. MUTTER	Report No. NAI TR 823.5/1, Mar 1962, 18 pp - tables, ONS Code 5010.11.842 - D/A Project 593-32-007,	Usclassified Meport A spectrographic-solution technique has been appl	to the analysis of certain iron, titanium, wanazum and zirconium alloys. The samples, after dissolution in an appropriate acid, are excited with a high-voltain an appropriate acid, are excited with a high-rolland and acid and acid and acid and acid acid acid acid acid acid acid aci	spark using a cornertial rotating-disk until Jureous, line parts are selected and calibration curres drawn line parts are selected and calibration curres drawn line parts are selected and calibration prepared from pure	metals. The coefficient of variation for analysis representative samples of each of the above alloy representative amountained	NO DISTRIBUTION LIMITATIONS		VATERIOUS OF A SPECTHOGRAPHIC-SOLUTION TECHN APPLICATIONS OF A SPECTHOGRAPHIC-SOLUTION TECHN APPLICATION OF HEMS. TITANIUM, WANABIUM, AND ZIEN TO ANALYSIS OF HEMS. TITANIUM, WANABIUM, AND ZIEN	MILLOTS - FFES - THE SEL S'1, March 1962, 18 pp - tables, Report No. Wal TH SEL S'1, March 1962, 18 pp - tables, OMS Code 5010, 11.842 - D'A Project 593-32-007,	Seclassified Report  A specingraphic-solution technique has been applied  A specingraphic solution technique has been applied  to the analysis of certain from, titanium, was addum  to the analysis of certain from.	and sirconium alloys. The semples, and an appropriate science are excited with a high-rollage in an appropriate scient forating-disk unit. Selfable	name paints are selected and calibration current parmy prepared from paints and calibration prepared from p	metals. The conflictest of values of allog forcesstative samples of each of the above allog representative samples.		NO DISTRIBUTION LIMITATIONS